Low cost photoelectron yield setup for surface process monitoring

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A low cost photoelectron yield setup for surface process monitoring

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Online monitoring of surface reactions allows an immediate quality control of surface preparations, both for scientific and high through put purposes. Several approaches for UHV process controlling with submonolayer sensitivity require cost-intensive instrumentation, such as a low energy electron microscope (LEEM)[1], a reflection high energy electron diffraction (RHEED)[2] unit or a photoemission electron microscope (PEEM)[3]. We report here a simple setup for controlling surface processes in vacua up to 1 mbar pressure. A pulsed ultra-violet (UV) light source is employed to probe the photoelectron yield which is closely related to the work function of the surface of interest. Our instrumentation is responsive to changes within the first atomic monolayer and is simple to be implemented in existing UHV preparation chamber systems. To benchmark its performance, a single layer of hexagonal-boron nitride (h-BN) was prepared on a Rh(111) surface[4] and its formation was monitored. The h-BN layer lowers the work function of the substrate from 4.9 eV[5] to 4.15 eV[6].

Figure 1 shows a scheme of the measurement setup. It consists of a pulsed Xe flash lamp for photoemission and a collector or a sample connection for the photocurrent measurement. The Xe lamp generates photons up to 5.6 eV, which is enough to prompt electron emission from most metal samples. The photocurrent noise FWHM is 0.42%, which translates to a work function noise of 16 meV for the preparation of h-BN on Rh(111).

We used a commercial Xe lamp (Ocean Optics) with two uncoated fused silica lenses and a sapphire window for coupling the light into the UHV chamber. The spot diameter on the sample was 6 mm and the pulse duration was 2.5 μs at 1/3 pulse height for wavelengths between 200 nm and 550 nm. The maximum repetition rate is 220 Hz and the pulse power variation is 1.2% FWHM as measured with a GaP photodiode. For the experiment shown in Figure 2, the flash rate was 10 Hz and each data point is the average of 16 light pulses. An aluminium sphere connected to an electrical feed through was used as an electron collector, which was biased with 9V batteries. To minimize effects on the electron trajectories due to non-constant electromagnetic fields, sample filament heating was separated from the UV excitation events in time. The measurement unit was an oscilloscope (Tektronix) and the synchronization of all events was triggered with a home-built 5V square pulse generator. The photocurrent can also be accessed by measuring the sample current (see Figure 1).

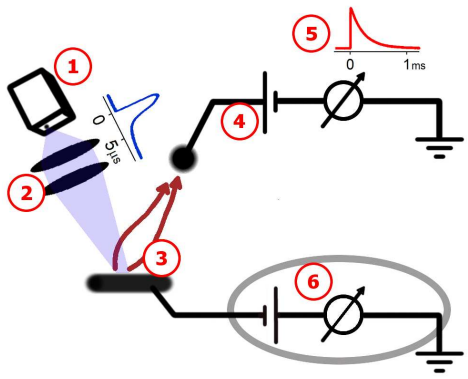

FIG. 1. Schematic overview of the equipment. The Xe flash lamp generates 2.5 μs UV light pulses (1), which were focused via fused silica lenses (2) and introduced into the UHV chamber through a sapphire viewport. On the sample, the light excites photoelectrons (3), which are collected with a biased aluminum sphere (4). The current measurement is achieved over the 1 MΩ resistance of an oscilloscope (5) with parallel capacities of the oscilloscope, the cable and of the sample-antenna capacitor, producing pulses with a decay time of 0.4 ms. Our setup did also allow to directly measure the total photoemission current from the sample (6), but this information is equivalent to that from the collector and the installation in the gray circle is optional.

Figure 2 shows the record of a boron nitride monolayer formation on a rhodium(111) single crystal[4]. Prior to preparation, the crystal had been cleaned by repetitive argon ion sputtering and oxygen annealing cycles. The sample was characterized by normal emission UV photoelectron spectroscopy (UPS) before and after the h-BN preparation with an apparatus described elsewhere[7]. In Figure 2, the collector current is shown, since this measurement is independent of sample connections and thus easier to be implemented in other systems. The collector bias induced an electric field of ∼2.8 V/cm, which allowed the detection of about 1/3 of the total emission current. The argon sputtered and oxygen cleaned rhodium single crystal showed a work function of 5.66 eV prior to the h-BN preparation. The first 20 mins of the preparation in Figure 2, are dominated by the work function fluctuations due to metal reduction and surface reorganization after sputtering. The chemical vapor deposition of the single layer h-BN starts at time zero with the application of 140 Langmuir borazine (1 L = 1 sec · 10^{-6} Torr),

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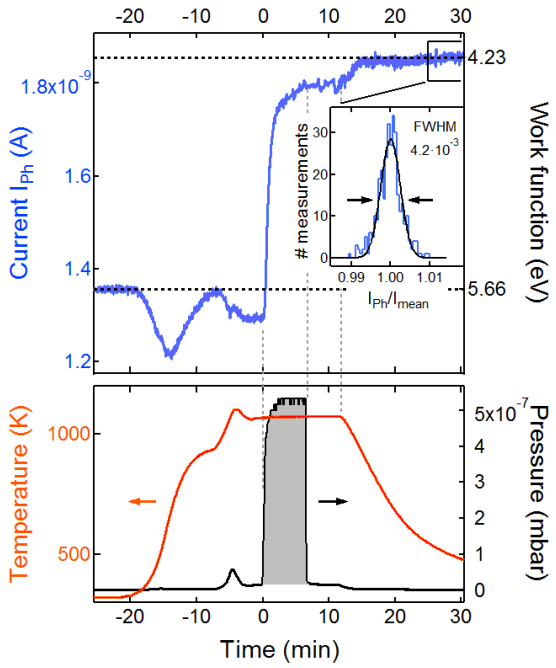

FIG. 2. The upper part shows the photocurrent ($\mathbf{I}_{Ph}$) during preparation as recorded by the collector. The pulse rate was 10 Hz and each data point is the average signal out of 16 flashing events. The black dotted lines and the right scale axis display the work function as determined by normal emission UPS measurements before and after preparation. Lower part: **Temperature** and **pressure** conditions for the h-BN preparation, the colored area in the pressure (**gray**) corresponds to 140L borazine.

as indicated by the gray pressure bar in the lower part of Figure 2. At the same time, a photo current increase of 38% is recorded, which corresponds to a work function shift of 1.43 eV. The relative FWHM scatter of the measurement after preparation is 0.42% within an interval of 6.4 minutes and a sampling dwell time of 1.2 seconds. This translates under the assumption of $\Delta I \propto -\Delta\Phi$ to a work function stability of ± 8 meV. This sensitivity allows precise insight into details of processes on surfaces. For example, the 2% yield increase upon cooling down the sample in Figure 2 at t = 11 - 14 min and temperatures above 960 K, implies a work function decrease of 84 meV. This might be explained by an h-BN layer relaxation towards the substrate.

The performance of the setup depends on the geometry and the pressure. Sample emission measurements at different argon pressures reveal the limiting conditions of the setup. Empirically, the sample photoelectron current is proportional to $I_0 e^{-\frac{p}{p_0}}$ with $p_0 = 0.4$ mbar. This defines the pressure dependence of the current measured and limits the application of the system to processes below 1 mbar. With a careful pressure handling, the setup achieved to monitor CVD processes up to 0.3 mbar.

We introduced a simple and inexpensive setup to monitor surface processes by measuring changes in photoelectron yield. It can monitor work function changes in the 10 meV range in real time. The setup works reliably at all probed sample temperatures and its pressure dependance is negligibly small below 2×10^{-3} mbar.

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